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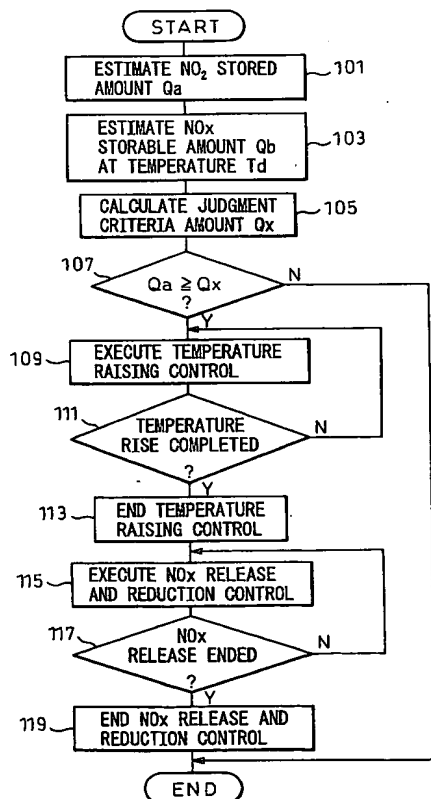
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(54) Title: EXHAUST PURIFICATION DEVICE AND EXHAUST PURIFICATION METHOD OF INTERNAL COMBUSTION ENGINE



(57) Abstract: A NO_x storing catalyst (11) comprising a precious metal catalyst (46) and NO_x absorbent (47) is arranged in an exhaust passage. When the air-fuel ratio of the exhaust gas is lean, the storing catalyst cold stores the NO₂ contained in the exhaust in the absorbent when the catalyst is inactive and hot stores the cold stored NO₂ in the absorbent when the catalyst is made active. The NO₂ contained in the exhaust is cold stored in the absorbent when the catalyst is not activated, and when a predetermined NO_x storing catalyst restoring condition (107) is met, a NO_x storing catalyst restoring control (109, 115) including raising the NO_x storing catalyst temperature to a predetermined temperature to activate it (109) is executed so as to restore the cold storing capability of the NO_x absorbent.



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DESCRIPTION

EXHAUST PURIFICATION DEVICE AND EXHAUST PURIFICATION
METHOD OF INTERNAL COMBUSTION ENGINE

5

TECHNICAL FIELD

The present invention relates to an exhaust
purification device and exhaust purification method of an
10 internal combustion engine.

BACKGROUND ART

As a catalyst for purifying NO_x contained in exhaust
gas when fuel is burned under a lean air-fuel ratio,
there is known a catalyst comprised of a carrier made of
15 alumina on the surface of which a layer of a NO_x
absorbent comprised of an alkali metal or alkali earth is
formed and on the surface of which a precious metal
catalyst such as platinum is carried (for example, see
Japanese Unexamined Patent Publication (Kokai) No. 6-
20 108826). In this catalyst, when the catalyst is activated
and the air-fuel ratio of the exhaust gas is lean, the
NO_x contained in the exhaust gas is stored in the NO_x
absorbent, while when the air-fuel ratio of the exhaust
gas is made rich, the NO_x which had been stored in the
25 NO_x absorbent is released and reduced.

However, this NO_x absorption and release action is
believed not to be performed when the catalyst is not
activated. Therefore, in the internal combustion engine
described in the above publication, when the catalyst is
30 not activated, the catalyst is heated by an electric
heater.

DISCLOSURE OF THE INVENTION

The inventors researched catalysts designed to
perform this NO_x absorption and release action and as a
35 result discovered that while the nitrogen monoxide NO
contained in exhaust gas is not stored in the NO_x
absorbent when the catalyst is not activated, nitrogen

dioxide NO_2 contained in exhaust gas is stored in the NO_x absorbent (cold stored) even when the catalyst is not activated by a mechanism different from that by which nitrogen monoxide NO is stored when the catalyst is
5 activated.

An object of the present invention is to provide an exhaust purification device and exhaust purification method designed to purify exhaust gas utilizing this fact discovered by the inventors.

10 According to a first aspect of the present invention, there is provided an exhaust purification device for an internal combustion engine having, a NO_x storing catalyst arranged in an engine exhaust passage, the NO_x storing catalyst being comprised of a precious
15 metal catalyst and a NO_x absorbent and, when an air-fuel ratio of inflowing exhaust gas is lean, cold storing nitrogen dioxide NO_2 contained in the exhaust gas in the NO_x absorbent when not activated and hot storing cold stored nitrogen dioxide NO_2 in the NO_x absorbent when
20 activated, the exhaust purification device for an internal combustion engine making the nitrogen dioxide NO_2 contained in the exhaust gas be cold stored in the NO_x absorbent in the state where the NO_x storing catalyst is not activated and executing a NO_x storing catalyst
25 restoring control including at least raising the temperature of the NO_x storing catalyst to a predetermined temperature to activate it when a predetermined NO_x storing catalyst restoring condition is met so as to restore the cold storing capability of the
30 NO_x absorbent in the state where the NO_x storing catalyst is not activated.

According this aspect of the invention, it is possible to remove the NO_2 in the exhaust gas even in the state where the NO_x storing catalyst is not activated.
35 Further, in this NO_x storing catalyst, if the NO_x storing catalyst is raised in temperature to be activated, the nitrogen dioxide cold stored when it was not activated is

released in the form of nitrogen monoxide NO, is oxidized to nitrogen dioxide NO₂ by the activated precious metal catalyst, and finally is hot stored in the NO_x absorbent in the form of nitric acid ions NO₃⁻. Therefore, by

5 raising the temperature of the NO_x storing catalyst to activate it, it is possible to restore the cold storing capability of the NO_x absorbent in the state where the NO_x storing catalyst is not activated. Accordingly, according to the first aspect of the present invention,

10 by suitably setting the NO_x storing catalyst restoring condition, it is possible to maintain the cold storing capability of the NO_x absorbent in the state where the NO_x storing catalyst is not activated. Note that when differentiation is particularly required in this

15 specification, the storing in the form of nitric acid ions NO₃⁻ will be referred to as "hot storing" and the storing in the form of nitrous acid NO₂⁻ will be referred to as "cold storing".

Preferably, the NO_x storing catalyst restoring

20 condition is set to be met before the cold storing capability of the NO_x absorbent in the state where the NO_x storing catalyst is not activated is saturated. According to this embodiment, by ensuring that the NO_x storing catalyst restoring control executes before the

25 cold storing capacity of the NO_x absorbent becomes saturated, it is possible to prevent the nitrogen dioxide NO₂ failed to be stored from being released into the atmosphere.

Preferably, the NO_x storing catalyst restoring

30 condition is set so that the cold stored nitrogen dioxide NO₂ will not be released from the NO_x absorbent in more than a predetermined amount when raising the temperature of and activating the NO_x storing catalyst in the NO_x storing catalyst restoring control.

35 As explained above, if raised in temperature and activated at the NO_x storing catalyst restoring control, the NO_x storing catalyst finally hot stores the nitrogen

dioxide NO_2 cold stored when it was not activated in the NO_x absorbent in the form of nitric acid ions NO_3^- . However, if the amount of the nitrogen dioxide NO_2 cold stored when not activated is greater than the amount of NO_x hot storable in the NO_x absorbent when raising the temperature of the NO_x storing catalyst to a predetermined temperature to activate it and is also greater than the amount of NO_x storable in the NO_x absorbent when raising the temperature of the NO_x storing catalyst to a predetermined temperature to activate it, part of the nitrogen dioxide NO_2 cold stored is liable to end up being unintentionally released in the form of NO_x when executing the NO_x storing catalyst restoring control.

According to this embodiment, this point is considered in setting the NO_x storing catalyst restoring condition, so when raising the temperature of the NO_x storing catalyst to activate it in the NO_x storing catalyst restoring control, it is possible to keep a large amount of cold stored nitrogen dioxide NO_2 from ending up being released unintentionally.

Note that here, "the cold stored nitrogen dioxide NO_2 not being released from the NO_x absorbent in more than a predetermined amount" includes not only the case of cold stored nitrogen dioxide NO_2 not being actually released in more than a predetermined amount as nitrogen oxides NO_x or not being released at more than a predetermined release speed, but also the case where the actual amount of release of nitrogen dioxide NO_2 per unit time calculated from the release speed of nitrogen oxides NO_x at the time when cold stored nitrogen dioxide NO_2 is released from the NO_x absorbent and the storing speed of nitrogen oxides NO_x in the NO_x absorbent is not more than a predetermined amount.

Preferably, the device has a NO_2 stored amount estimating means for estimating an amount of nitrogen dioxide NO_2 cold stored in the NO_x absorbent and a NO_x

storable amount estimating means for estimating an amount of nitrogen oxides NO_x able to be stored in the NO_x absorbent when the NO_x storing catalyst is at the predetermined temperature, and the NO_x storing catalyst restoring condition is deemed to be met when the NO_2 stored amount estimated by the NO_2 stored amount estimating means becomes greater than or equal to a predetermined amount set to not more than the NO_x storable amount based on the NO_x storable amount estimated by the NO_x storable amount estimating means.

As explained above, when for example the amount of the nitrogen dioxide NO_2 cold stored in the NO_x absorbent is greater than the amount of nitrogen oxides NO_x able to be cold stored in the NO_x absorbent when the temperature of the NO_x storing catalyst is the predetermined temperature, part of the cold stored nitrogen dioxide NO_2 may fail to be stored in the NO_x absorbent and end up being released as NO_x when raising the temperature of the NO_x storing catalyst to activate it in the NO_x storing catalyst restoring control.

As opposed to this, in this embodiment, since the NO_x storing catalyst restoring condition is deemed to be met and the NO_x storing catalyst restoring control is executed when the NO_2 stored amount estimated by the NO_2 stored amount estimating means becomes greater than or equal to a predetermined amount set to not more than the NO_x storable amount based on the NO_x storable amount estimated by the NO_x storable amount estimating means, it is possible to keep the cold stored nitrogen dioxide NO_2 from being released when raising the temperature of the NO_x storing catalyst to activate it in the NO_x storing catalyst restoring control.

Preferably, the NO_x storing catalyst is a NO_x storing catalyst having the function of hot storing nitrogen oxides NO_x contained in exhaust gas in the NO_x absorbent when the NO_x storing catalyst is activated and the air-fuel ratio of the exhaust gas flowing into the

NO_x storing catalyst is lean, the device has a NO_x release speed estimating means for estimating a release speed of nitrogen oxides NO_x from the NO_x absorbent when making the NO_x storing catalyst the predetermined temperature and a NO_x storing speed estimating means for estimating a storing speed of nitrogen oxides NO_x to the NO_x absorbent when making the NO_x storing catalyst the predetermined temperature, and the NO_x storing catalyst restoring condition is deemed to be met when the NO_x release speed estimated by the NO_x release speed estimating means becomes greater than or equal to a predetermined speed set to not more than the NO_x storing speed based on the NO_x storing speed estimated by the NO_x storing speed estimating means.

If the release speed of nitrogen oxides NO_x when cold stored nitrogen dioxide NO₂ is released from the NO_x absorbent when making the temperature of the NO_x storing catalyst the predetermined temperature is less than the storing speed of nitrogen oxides NO_x to the NO_x absorbent when making the temperature of the NO_x storing catalyst the predetermined temperature, it is conceivable that no cold stored nitrogen dioxide NO₂ will substantially be released when raising the temperature of the NO_x storing catalyst to the predetermined temperature to activate it in the NO_x storing catalyst restoring control.

This embodiment was made in consideration of this. When the NO_x release speed estimated by the NO_x release speed estimating means becomes greater than or equal to a predetermined speed set to not more than the NO_x storing speed based on the NO_x storing speed estimated by the NO_x storing speed estimating means, it is deemed that the NO_x storing catalyst restoring condition is met and the NO_x storing catalyst restoring control is executed. Due to this, it is possible to substantially keep the cold stored nitrogen dioxide NO₂ from being released from the NO_x absorbent when raising the temperature of the NO_x storing catalyst to activate it in the NO_x storing

catalyst restoring control and as a result keep the stored nitrogen dioxide NO_2 from ending up being released into the atmosphere as NO_x .

Preferably, the NO_x storing catalyst is a NO_x storing catalyst having the function of hot storing nitrogen oxides NO_x contained in exhaust gas in the NO_x absorbent when the NO_x storing catalyst is activated and the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst is lean, the device has a NO_x release speed estimating means for estimating a release speed of nitrogen oxides NO_x from the NO_x absorbent when making the NO_x storing catalyst the predetermined temperature, a NO_x exhaust speed estimating means for estimating an exhaust speed of nitrogen oxides NO_x from the internal combustion engine, and a NO_x storing speed estimating means for estimating a storing speed of nitrogen oxides NO_x to the NO_x absorbent when making the NO_x storing catalyst the predetermined temperature, and the NO_x storing catalyst restoring condition is deemed to be met when a sum of the NO_x release speed estimated by the NO_x release speed estimating means and the NO_x exhaust speed estimated by the NO_x exhaust speed estimating means becomes greater than or equal to a predetermined speed set to not more than the NO_x storing speed based on the NO_x storing speed estimated by the NO_x storing speed estimating means.

For example, if the release speed of nitrogen oxides NO_x when cold stored nitrogen dioxide NO_2 is released from the NO_x absorbent when making the temperature of the NO_x storing catalyst the predetermined temperature is the same as the storing speed of nitrogen oxides NO_x to the NO_x absorbent when making the temperature of the NO_x storing catalyst the predetermined temperature, it is conceivable that no cold stored nitrogen dioxide NO_2 will be released when raising the temperature of the NO_x storing catalyst to the predetermined temperature to activate it in the NO_x storing catalyst restoring

control. However, in this case, the nitrogen oxides NO_x exhausted from the internal combustion engine will end up being released into the atmosphere as they are during the NO_x storing catalyst restoring control.

5 As opposed to this, according to this embodiment, when the sum of the NO_x release speed estimated by the NO_x release speed estimating means and the NO_x exhaust speed estimated by the NO_x exhaust speed estimating means becomes greater than or equal to a predetermined speed
10 set to not more than the NO_x storing speed based on the NO_x storing speed estimated by the NO_x storing speed estimating means, it is deemed that the NO_x storing catalyst restoring condition is met and the NO_x storing catalyst restoring control is executed, so it is possible
15 to keep the nitrogen oxides NO_x exhausted from the internal combustion engine from being released into the atmosphere at the time of the NO_x storing catalyst restoring control.

 Preferably, the NO_x storing catalyst has the
20 function of releasing, reducing, and purifying the nitrogen oxides NO_x which had been hot stored in the NO_x absorbent when the NO_x storing catalyst is activated and when making the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst smaller and establishing
25 the presence of a reducing agent in state, and the NO_x storing catalyst restoring control includes making the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst smaller and establishing the presence of a reducing agent in state. According to this embodiment,
30 by performing the NO_x storing catalyst restoring control, it is possible to release, reduce, and purify the nitrogen oxides NO_x hot stored in the NO_x absorbent.

 Preferably, the device further has a NO_2 ratio increasing means for increasing a ratio of nitrogen
35 dioxide NO_2 with respect to nitrogen monoxide NO produced at the time of combustion under a lean air-fuel ratio when the NO_x storing catalyst is not activated compared

with when the NO_x storing catalyst is activated in the same engine operating state.

5 The NO_x storing catalyst can cold store nitrogen dioxide NO₂ in the NO_x absorbent even when not activated when the air-fuel ratio of the inflowing exhaust gas is lean. Therefore, according to this embodiment, it is possible to improve the NO_x purification rate when the NO_x storing catalyst is not activated.

10 According to a second aspect of the invention, there is provided an exhaust purification method for an internal combustion engine including, arranging a NO_x storing catalyst in an engine exhaust passage, the NO_x storing catalyst being comprised of a precious metal catalyst and a NO_x absorbent and, when an air-fuel ratio
15 of inflowing exhaust gas is lean, cold storing nitrogen dioxide NO₂ contained in the exhaust gas in the NO_x absorbent when not activated and hot storing cold stored nitrogen dioxide NO₂ in the NO_x absorbent when activated, making the nitrogen dioxide NO₂ contained in the exhaust
20 gas be cold stored in the NO_x absorbent in the state where the NO_x storing catalyst is not activated and raising the temperature of the NO_x storing catalyst to a predetermined temperature to activate it so as to restore the cold storing capability of the NO_x absorbent in the
25 state where the NO_x storing catalyst is not activated before the cold storing capability of the NO_x absorbent in the state where the NO_x storing catalyst is not activated is saturated.

30 According to the second aspect of the invention, it is possible to remove NO₂ in the exhaust gas even when the NO_x storing catalyst is not activated. Further, in the NO_x storing catalyst, when the NO_x storing catalyst is raised in temperature to be activated, the nitrogen dioxide NO₂ cold stored when not activated is finally hot
35 stored in the NO_x absorbent in the form of nitric acid ions NO₃⁻, so the cold storing capability of the NO_x absorbent in the state where the NO_x storing catalyst is

not activated can be restored. Accordingly, according to this aspect of the invention, the cold storing capacity of the NO_x absorbent in the state where the NO_x storing catalyst is not activated can be maintained.

5 BRIEF DESCRIPTION OF DRAWINGS

These and other objects and features of the present invention will become clearer from the following description of the preferred embodiments given with reference to the attached drawings, wherein:

10 FIG. 1 shows the case of application of the present invention to a compression ignition type internal combustion engine;

15 FIGS. 2a and 2b are views schematically showing cross-sections of the carrier surface part of a NO_x storing catalyst;

FIG. 3 is a view for explaining a seepage phenomenon;

20 FIG. 4 is a view of the relationship between a NO_x storable amount Ab and a temperature TC of a NO_x storing catalyst;

FIG. 5 is a flow chart of a control routine of a method workable by the configuration shown in FIG. 1;

FIG. 6 is a view of various injection patterns of fuel;

25 FIG. 7 is a flow chart of a control routine of another method workable by the configuration shown in FIG. 1;

30 FIG. 8a is a view of the relationship between a NO_x release speed and a NO_x stored amount, while FIG. 8b is a view of the relationship between a NO_x storing speed and a NO_x stored amount;

FIG. 9 is a flow chart of a control routine of still another method workable by the configuration shown in FIG. 1; and

35 FIG. 10 is an explanatory view illustrating the relationship among a NO_x release speed Va from a NO_x absorbent, a NO_x exhaust speed Ve from the engine, a NO_x

storing speed V_b to the NO_x absorbent, a judgment criteria speed V_x , etc. using as the abscissa the NO_2 stored amount Q_a of the NO_x absorbent.

BEST MODES FOR CARRYING OUT THE INVENTION

5 Preferred embodiments of the present invention will be described in detail below while referring to the attached figures.

FIG. 1 shows the case of application of the present invention to a compression ignition type internal
10 combustion engine. Note that the present invention may also be applied to a spark ignition type internal combustion engine.

Referring to FIG. 1, 1 indicates an engine body, 2 indicates a combustion chamber of each cylinder, 3 indicates an electronically controlled fuel injector for injecting fuel into each combustion chamber 2, 4 indicates an intake manifold, and 5 indicates an exhaust manifold. The intake manifold 4 is connected through an intake duct 6 to an outlet of a compressor 7a of an exhaust turbocharger 7. The inlet of the compressor 7a is
20 connected to an air cleaner 8. Inside the intake duct 6 is arranged a throttle valve 9 driven by a step motor. Further, around the intake duct 6 is arranged a cooling device (intercooler) 10 for cooling the intake air flowing through the inside of the intake duct 6. In the embodiment shown in FIG. 1, the engine cooling water is guided into the intercooler 10. The engine cooling water cools the intake air. On the other hand, the exhaust manifold 5 is connected to an inlet of an exhaust turbine 7b of the exhaust turbocharger 7, while the outlet of the exhaust turbine 7b is connected to a casing 12 housing a NO_x storing catalyst 11. The header outlet of the exhaust manifold 5 is provided with a reducing agent supply valve 13 for supplying a reducing agent comprised of for
30 example a hydrocarbon into the exhaust gas flowing through the inside of the exhaust manifold 5.

The exhaust manifold 5 and the intake manifold 4 are

linked together through an exhaust gas recirculation (hereinafter referred to as an "EGR") passage 14. The EGR passage 14 is provided with an electronically controlled EGR control valve 15. Further, around the EGR passage 14 is arranged a cooling device (EGR cooler) 16 for cooling the EGR gas flowing through the inside of the EGR passage 14. In the embodiment shown in FIG. 1, the engine cooling water is guided into the EGR cooler 16. The engine cooling water cools the EGR gas. On the other hand, each fuel injector 3 is linked through a fuel feed tube 17 to a fuel reservoir, that is, a so-called "common rail" 18. This common rail 18 is supplied with fuel from an electronically controlled variable discharge fuel pump 19. The fuel supplied into the common rail 18 is supplied through each fuel feed tube 17 to the fuel injector 3.

An electronic control unit 30 is comprised of a digital computer provided with a read only memory (ROM) 32, a random access memory (RAM) 33, a microprocessor (CPU) 34, an input port 35, and an output port 36 all connected to each other by a bidirectional bus 31. The NO_x storing catalyst 11 is provided with a temperature sensor 20 for detecting the temperature of the NO_x storing catalyst 11. The output signal of the temperature sensor 20 is input to the input port 35 through a corresponding AD converter 37. Further, an accelerator pedal 40 is connected to a load sensor 41 generating an output voltage proportional to the amount of depression L of the accelerator pedal 40. The output voltage of the load sensor 41 is input to the input port 35 through a corresponding AD converter 37. Further, the input port 35 has a crank angle sensor 42 generating an output pulse each time the crankshaft turns for example by 15 degrees connected to it. On the other hand, the output port 36 is connected through corresponding drive circuits 38 to the fuel injectors 3, throttle valve 9 step motor, reducing agent supply valve 13, EGR control valve 15, and fuel pump 19.

The NO_x storing catalyst 11 shown in FIG. 1 is comprised of a monolithic catalyst. A base of the NO_x storing catalyst 11 carries for example a catalyst carrier comprised of alumina. FIGS. 2a and 2b schematically show the cross-section of the surface part of this catalyst carrier 45. As shown in FIGS. 2a and 2b, the catalyst carrier 45 carries a precious metal catalyst 46 dispersed on its surface. Further, the catalyst carrier 45 is formed with a layer of a NO_x absorbent 47 on its surface.

In this embodiment of the present invention, platinum Pt is used as the precious metal catalyst 46. As the ingredient forming the NO_x absorbent 47, for example, at least one element selected from potassium K, sodium Na, cesium Cs, or another alkali metal, barium Ba, calcium Ca, or another alkali earth, lanthanum La, yttrium Y, or another rare earth may be used.

If the ratio of the air and fuel (hydrocarbons) supplied to the engine intake passage, combustion chambers 2, and exhaust passage upstream of the NO_x storing catalyst 11 is referred to as the "air-fuel ratio of the exhaust gas", when the precious metal catalyst 46 is activated, that is, when the NO_x storing catalyst 11 is activated, the NO_x absorbent 47 performs a NO_x absorption and release action of hot storing the NO_x when the air-fuel ratio of the exhaust gas is lean and releasing the hot stored NO_x when the oxygen concentration in the exhaust gas falls. Note that when fuel (hydrocarbons) or air is not being supplied to the exhaust passage upstream of the NO_x storing catalyst 11, the air-fuel ratio of the exhaust gas matches the air-fuel ratio of the air-fuel mixture supplied to the combustion chambers 2. Therefore, in this case, the NO_x absorbent 47 hot stores NO_x when the air-fuel ratio of the air-fuel mixture supplied into the combustion chambers 2 is lean, while releases the hot stored NO_x when the oxygen concentration in the air-fuel mixture

supplied to the combustion chambers 2 falls.

That is, if explaining this taking as an example the case of using barium Ba as the ingredient forming the NO_x absorbent 47, when the air-fuel ratio of the exhaust gas is lean, that is, when the oxygen concentration in the exhaust gas is high, if the precious metal catalyst 46 is activated, the NO contained in the exhaust gas is oxidized on the platinum Pt 46 such as shown in FIG. 2a to become NO_2 , then is absorbed in the NO_x absorbent 47 and disperses in the NO_x absorbent 47 in the form of nitric acid ions NO_3^- while bonding with the barium oxide BaO. In this way, the NO_x is hot stored in the NO_x absorbent 47. That is, storing in the form of nitric acid ions NO_3^- is referred to as "hot storing". So long as the oxygen concentration in the exhaust gas is high, NO_2 is produced on the surface of the platinum Pt 46. So long as the hot storing capacity of the NO_x absorbent 47 is not saturated, the NO_2 is hot stored in the NO_x absorbent 47 and nitric acid ions NO_3^- are produced.

As opposed to this, by making the air-fuel ratio in the combustion chambers 2 rich or the stoichiometric air-fuel ratio or by supplying a reducing agent from the reducing agent supply valve 13 so as to make the air-fuel ratio of the exhaust gas rich or the stoichiometric air-fuel ratio, the oxygen concentration in the exhaust gas falls, so the reaction proceeds in the reverse direction ($\text{NO}_3^- \rightarrow \text{NO}_2$) and therefore the nitric acid ions NO_3^- in the NO_x absorbent 47 are released from the NO_x absorbent 47 in the form of NO_2 , NO, etc. In this case, since the reducing agent (unburned HC, CO, etc.) is present in the exhaust gas, the released NO_x is reduced by the reducing agent (unburned HC, CO, etc.) contained in the exhaust gas.

Now, the nitrogen oxides NO_x in the exhaust gas are not hot stored in the NO_x absorbent 47 in the form of nitrogen monoxide NO. They have to be converted to the form of nitrogen dioxide NO_2 or else will not be hot

stored in the NO_x absorbent 47. That is, the nitrogen monoxide NO contained in the exhaust gas has to be converted to nitrogen dioxide NO_2 , that is, has to be oxidized, or will not be hot stored in the NO_x absorbent 47. The platinum Pt 46 inherently has activity at a low temperature. However, the basicity of the NO_x absorbent 47 is considerably strong. Therefore, the activity of the platinum Pt 46 at a low temperature, that is, the acidity, ends up becoming weak. As a result, if the temperature TC of the NO_x storing catalyst 11 falls, the action of oxidation of the nitrogen monoxide NO to nitrogen dioxide becomes weaker. Therefore, to oxidize the nitrogen monoxide NO , it is necessary that the precious metal catalyst 46 be high in temperature and activated, that is, that the NO_x storing catalyst 11 be activated. Therefore, up to now, to purify NO_x , it had been considered necessary that the precious metal catalyst 46 be activated, that is, that the NO_x storing catalyst 11 be activated.

The inventors engaged in research on this NO_x storing catalyst 11 and as a result learned that the nitrogen monoxide NO contained in the exhaust gas will not be stored in the NO_x absorbent 47 until the platinum Pt 46 is activated, that is, unless the NO_x storing catalyst 11 is activated, but nitrogen dioxide NO_2 will be cold stored in the NO_x absorbent 47 in the form of nitrous acid NO_2^- as shown in FIG. 2b even if the NO_x storing catalyst 11 is not activated. Note that in this specification, the storage in the form of nitrous acid NO_2^- will be referred to as "cold storing" to differentiate it from the above "hot storing". Further, when it is not necessary to particularly differentiate the hot storing and cold storing, "storing" will be simply referred to.

Further, since cold storing of NO_2 is possible even if the NO_x storing catalyst 11 is not activated, the "activation of the NO_x storing catalyst 11" in this

specification means a state where nitrogen monoxide NO can be oxidized to nitrogen dioxide NO₂ and hot stored in the NO_x absorbent 47 when the air-fuel ratio of the inflowing exhaust gas is lean and further a state where the NO_x stored in the NO_x absorbent 47 can be released and reduced if reducing the air-fuel ratio of the inflowing exhaust gas (that is, making it rich or the stoichiometric air-fuel ratio) and establishing the presence of a reducing agent.

10 In this way, the nitrogen dioxide NO₂ is cold stored even if the NO_x storing catalyst 11 is not activated, so in this embodiment of the present invention, the nitrogen dioxide NO₂ contained in the exhaust gas is made to be cold stored in the NO_x absorbent in the state where the NO_x storing catalyst 11 is not activated when the air-fuel ratio of the inflowing exhaust gas is lean and, for example, when the fuel is being burned under a lean air-fuel ratio. That is, in the compression ignition type internal combustion engine such as shown in FIG. 1, the air-fuel ratio of the exhaust gas is lean at the time of normal operation. Further, in this embodiment of the present invention, if not performing control for raising the temperature of the NO_x storing catalyst 11 as explained later (temperature raising control), the NO_x storing catalyst 11 is not activated. Therefore, at the time of normal operation, the NO_x absorbent 47 of the NO_x storing catalyst 11 cold stores the nitrogen dioxide NO₂ contained in the exhaust gas.

30 However, if the operation where the air-fuel ratio of the exhaust gas is lean continues to be performed in the state where the NO_x storing catalyst 11 is not activated, the cold storing capability (NO₂ storing capability) of the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated will end up being saturated and therefore NO₂ will end up no longer being able to be cold stored by the NO_x absorbent 47. Therefore, in this embodiment of the present invention,

the NO_x storing catalyst 11 is raised in temperature to activate it and restore the cold storing capability of the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated before the cold storing capability of the NO_x absorbent 47 becomes saturated.

That is, in the above way, when the NO_x storing catalyst 11 is not activated, as shown in FIG. 2b, the nitrogen dioxide NO₂ contained in the exhaust gas is cold stored in the NO_x absorbent 47. Further, if the temperature TC of the NO_x storing catalyst 11 rises in this state, the nitrogen dioxide NO₂ which had been cold stored in the NO_x absorbent 47 will be released in the form of nitrogen monoxide NO, will be oxidized to nitrogen dioxide NO₂ by the activated precious metal catalyst 46, and will be hot stored in the NO_x absorbent 47. Therefore, when the NO_x storing catalyst 11 is activated, the cold stored nitrogen dioxide NO₂ is hot stored in the NO_x absorbent 47 in the form of nitric acid ions NO₃⁻. Further, when the nitrogen dioxide NO₂ cold stored when it was not activated in this way is hot stored in the NO_x absorbent in the form of nitric acid ions NO₃⁻, the cold storing capacity of the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated is recovered, that is, restored.

Utilizing this action, in this embodiment of the present invention, for example, when having the nitrogen dioxide NO₂ be cold stored in the NO_x absorbent 47 in the state not activated, by repeatedly raising the temperature of the NO_x storing catalyst 11 to activate it and then returning it to the inactive state, that is, by periodically raising the temperature of the NO_x storing catalyst 11 and activating it, it is possible to restore and maintain the cold storing capability of the NO_x absorbent 47. That is, in this case, raising the temperature of the NO_x storing catalyst 11 to activate it forms a control for restoring the NO_x storing catalyst (NO_x storing catalyst restoring control). Note that the

specific temperature TC of the NO_x storing catalyst 11 in this case is for example 100 to 150°C in the case of cold storing the nitrogen dioxide NO₂ in the nonactivated state and 300 to 400°C in the case of raising the catalyst in temperature to activate it. As explained later, the NO_x storing catalyst 11 is gradually activated by this temperature rise and along with this the ratio of the hot storing to the storing action as a whole increases. Therefore, in the above-mentioned case, when raising the temperature of the NO_x storing catalyst 11 to activate it and cause hot storing of the cold stored nitrogen dioxide NO₂, it is preferable to sufficiently raise the temperature of the NO_x storing catalyst 11 to activate it. For this, it is preferable to raise the temperature of the NO_x storing catalyst 11 to activate it so that at least for example the ratio of the hot storing becomes greater than or equal to the ratio of the cold storing.

However, as explained above, the nitrogen dioxide NO₂ cold stored in the NO_x absorbent 47 when the NO_x storing catalyst 11 is not activated can be finally hot stored in the NO_x absorbent 47 in the form of nitric acid ions NO₃⁻ by raising the temperature of the NO_x storing catalyst 11 to activate it. Further, as explained above, the NO_x hot stored in the NO_x absorbent 47 in this way is released and reduced by making the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst 11 smaller (that is, making it rich or the stoichiometric air-fuel ratio) and establishing the presence of a reducing agent in the state where the NO_x storing catalyst 11 is activated.

Due to the above, in this embodiment of the present invention, when the NO_x storing catalyst 11 is not activated, the nitrogen dioxide NO₂ contained in the exhaust gas is cold stored in the NO_x absorbent 47. Then, after being used for a certain period, the temperature of the NO_x storing catalyst 11 is raised to activate it so

as to cause the cold stored nitrogen dioxide NO_2 to be hot absorbed in the NO_x absorbent 47 before the cold storing capability of the NO_x absorbent 47 becomes saturated. Further, the air-fuel ratio of the inflowing exhaust gas is made smaller and a reducing agent made present in state so as to release and reduce the hot stored nitrogen dioxide NO_2 . By this method, it is possible to purify the nitrogen dioxide NO_2 in the exhaust gas and suppress the release of nitrogen oxides NO_x into the atmosphere.

On the other hand, in the case of actually working the above method, when raising the temperature of the NO_x storing catalyst 11 to activate it, the phenomenon of the cold stored nitrogen dioxide NO_2 ending up being released from the NO_x absorbent 47 unintentionally (hereinafter called the "seepage phenomenon") sometimes occurs. Further, this seepage phenomenon occurs only when the amount of nitrogen dioxide NO_2 cold stored when the NO_x storing catalyst 11 is not activated is large. Note that in this case, the cold stored nitrogen dioxide NO_2 is released in the form of NO or NO_2 etc. (NO_x).

FIG. 3 is a view of this phenomenon and shows the change in the NO_x concentration Oc in the NO_x storing catalyst outflowing exhaust gas in the case of raising the temperature of the NO_x storing catalyst 11. The abscissa shows the temperature TC of the NO_x storing catalyst 11, while the ordinate shows the NO_x concentration in the exhaust gas flowing out from the NO_x storing catalyst 11. In the figure, the solid line shows the case of a large amount of nitrogen dioxide NO_2 cold stored when the NO_x storing catalyst 11 is not activated, while the broken line shows the case of a small amount of nitrogen dioxide NO_2 cold stored when the NO_x storing catalyst 11 is not activated. Further, the NO_x concentration Ic shows the NO_x concentration in exhaust gas flowing into the NO_x storing catalyst 11.

As seen in FIG. 3, when the amount of cold stored

nitrogen dioxide NO_2 is large, sometimes the NO_x concentration in the exhaust gas flowing out from the NO_x storing catalyst 11 will become greater than the NO_x concentration in the exhaust gas flowing in during the process of temperature rise. That is, when the amount of cold stored nitrogen dioxide NO_2 is great, the cold stored nitrogen dioxide NO_2 is released in the process of temperature rise.

Further, this seepage phenomenon is believed to occur since the NO_x storable amount of the NO_x absorbent 47 is greater before the rise in temperature, that is, when the NO_x storing catalyst 11 is not activated, than after the rise in temperature, that is, when the NO_x storing catalyst 11 is activated. That is, the relationship between the NO_x storable amount A_b (including cold storable amount (NO_2 storable amount) of NO_x absorbent 47 when the NO_x storing catalyst 11 is not activated) and the temperature TC of the NO_x storing catalyst 11 before and after activation of the NO_x storing catalyst 11 is believed to become that as shown in FIG. 4. In the figure, the solid line shows the NO_x storable amount A_b , while the broken line shows the hot storable amount in this. That is, the NO_x storable amount A_b of the NO_x absorbent 47 declines along with a rise of the temperature TC , while the hot storable amount rises along with a rise in the temperature TC , becomes maximum at the time of a certain temperature T_a , then declines along with a rise in the temperature TC .

Further, the ratio of the hot storable amount in the NO_x storable amount A_b increases along with a rise in the temperature TC . At the above temperature T_a or more, the NO_x storable amount A_b and the hot storable amount become substantially equal. That is, at the cold side, mainly cold storing is performed. When the temperature TC rises and the NO_x storing catalyst 11 becomes active, the ratio of hot storing gradually increases. At the hot side, mainly hot storing is performed. That is, in this

embodiment of the present invention, specifically, cold storing is performed even when the NO_x storing catalyst 11 is activated. Therefore, for example, the expression of "cold storing when the NO_x storing catalyst 11 is not activated" or "hot storing when the NO_x storing catalyst 11 is not activated" is intended to merely simplify the expression and is not intended to exclude the case of cold storing when the NO_x storing catalyst is activated.

Now, as shown in FIG. 4, the NO_x storable amount of the NO_x absorbent 47 declines along with a rise of the temperature TC. In such a case, for example, when the NO_x storing catalyst 11 is not activated (that is, before the rise in temperature), if the amount of cold stored nitrogen dioxide NO₂ is greater than the amount of storable NO_x at the temperature after the temperature rise, part of the cold stored nitrogen dioxide NO₂ will fail to be stored and will be released. The above-mentioned seepage phenomenon is believed to occur due to this.

Below, the method of suppressing the occurrence of the seepage phenomenon explained above and using the NO_x storing catalyst 11 to purify the NO₂ in the exhaust gas and suppress release of NO_x into the atmosphere will be explained.

FIG. 5 is a flow chart showing the control routine of a method able to be worked by the configuration shown in FIG. 1. This control routine is executed by interruption every certain time by the ECU 30 at the time of normal operation of the engine. As explained above, in a compression ignition type internal combustion engine such as shown in FIG. 1, the exhaust gas air-fuel ratio is lean at the time of normal operation. Further, the NO_x storing catalyst 11 is in a not activated state. Therefore, the NO_x absorbent 47 of the NO_x storing catalyst 11 cold stores the nitrogen dioxide NO₂ contained in the exhaust gas.

When this control routine shown in FIG. 5 starts,

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first, at step 101, the NO₂ stored amount Qa at that point of time is estimated. This NO₂ stored amount Qa is estimated based on for example the type of the NO_x storing catalyst 11 and the history of the operating state from when the previous NO_x release and reducing control (explained later) ended. In this case, for example, the engine speed and fuel injection amount are used as indicators expressing the operating state. The NO₂ storing speed (amount of NO₂ stored per unit time) to the NO_x absorbent 47 in each operating state expressed by these is found in advance by experiments etc. and stored as a map. The map is used to find the NO_x stored amount Qa based on the history of the operating state. Note that if considering the effect of the temperature TC of the NO_x storing catalyst 11 on the NO₂ storing speed, it is possible to find the NO₂ stored amount Qa more accurately.

When the NO₂ stored amount Qa is estimated at step 101, the routine proceeds to step 103. At step 103, the NO_x storable amount Qb of the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is the predetermined temperature Td is estimated. Here, this temperature Td is a temperature predetermined as the temperature for performing the later explained NO_x release and reducing control and is greater than or equal to the temperature where the NO_x storing catalyst 11 at least starts to be activated (activation temperature). Most preferable as the temperature Td is the temperature at which the release and reduction of the NO_x become most active.

The NO_x storable amount Qb is estimated for example based on the type of the NO_x storing catalyst 11 and the temperature Td. That is, for example, the relationship between the temperature TC of the NO_x storing catalyst 11 and the NO_x storable amount Qb is found in advance by experiments etc. and stored in a map. This map is used to find the NO_x storable amount Qb corresponding to the

above temperature T_d .

When the NO_x storable amount Q_b is estimated at step 103, at the next step 105, the judgment criteria amount Q_x is calculated based on the NO_x storable amount Q_b .

5 This judgment criteria amount Q_x is used in the following step 107 and for example is found by the equation $Q_x = Q_b - \alpha$ (where $\alpha \geq 0$). Here, the constant α is a safety margin for suppressing occurrence of the above seepage phenomenon and can be suitably set.

10 When the judgment criteria amount Q_x is calculated at step 105, at the next step 107, it is judged if the NO_2 stored amount Q_a is the judgment criteria amount Q_x or more. When it is judged here that the NO_2 stored amount Q_a is less than the judgment criteria amount Q_x ,
15 this control routine ends and the engine continues normal operation. On the other hand, when it is judged that the NO_2 stored amount Q_a is the judgment criteria amount Q_x or more, the routine proceeds to step 109 where a temperature raising control is executed.

20 The temperature raising control performed at step 109 is control for raising the temperature T_c of the NO_x storing catalyst 11 to the above-mentioned temperature T_d . In the present embodiment, this temperature raising control is performed by control of the fuel injection
25 pattern as explained below. That is, FIG. 6 is a schematic view showing four examples of fuel injection patterns able to be used in the internal combustion engine shown in FIG. 1. Usually, the main fuel q_m is injected near compression top dead center as shown in (I)
30 in FIG. 6. As opposed to this, if the temperature raising control is started at step 109, for example, the fuel injection pattern shown in (II) of FIG. 6 is used. That is, the injection timing of the main fuel q_m is delayed to after compression top dead center. If the injection
35 timing of the main fuel q_m is delayed to after compression top dead center in this way, the after burning period becomes longer and therefore the exhaust

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gas temperature rises. If the exhaust gas temperature rises, the temperature TC of the NO_x storing catalyst 11 rises along with this.

Further, to raise the temperature TC of the NO_x storing catalyst 11, it is also possible to inject auxiliary fuel qv near suction top dead center in addition to the main fuel qm as shown in (III) of FIG. 6. If additionally injecting auxiliary fuel qv in this way, the fuel to be burned increases by exactly the auxiliary fuel qv, so the exhaust gas temperature rises and therefore the temperature TC of the NO_x storing catalyst 11 rises.

On the other hand, if injecting auxiliary fuel qv near suction top dead center in this way, due to the heat of compression during the compression stroke, aldehydes, ketones, peroxides, carbon monoxide, and other intermediate products are produced from the auxiliary fuel qv. These intermediate products accelerate the reaction of the main fuel qm. Therefore, in this case, as shown in (III) of FIG. 6, even if the injection timing of the main fuel qm is greatly delayed, good combustion can be obtained without causing misfires. That is, it is possible to greatly delay the injection timing of the main fuel qm, so the exhaust gas temperature becomes considerably high and accordingly the temperature TC of the NO_x storing catalyst 11 can be quickly raised.

Further, to raise the temperature TC of the NO_x storing catalyst 11, it is possible to inject auxiliary fuel qp during the expansion stroke or the exhaust stroke in addition to the main fuel qm as shown in (IV) of FIG. 6. That is, in this case, the majority of the auxiliary fuel qp is exhausted to the inside of the exhaust passage in the form of unburned HC without being burned. This unburned HC is oxidized by the surplus oxygen on the NO_x storing catalyst 11. The heat of the oxidation reaction produced at this time causes the temperature TC of the NO_x storing catalyst 11 to rise.

Note that in this embodiment of the present invention, the fuel injection pattern is controlled in the temperature raising control so as to maintain the air-fuel ratio of the exhaust gas in the lean state. This is because if the air-fuel ratio of the exhaust gas becomes rich or the stoichiometric air-fuel ratio in the temperature raising process, the cold stored NO_2 is liable to end up being released. In the temperature raising process, the temperature TC of the NO_x storing catalyst 11 does not rise sufficiently, so reduction and purification are not possible when the cold stored NO_2 is released.

As explained above, when the NO_x storing catalyst 11 is raised in temperature and activated by the temperature raising control, the nitrogen dioxide NO_2 cold stored in the NO_x absorbent 47 before the NO_x storing catalyst 11 was raised in temperature, that is, when it was still not activated, is finally hot stored in the NO_x absorbent 47 in the form of nitric acid ions NO_3^- .

In this embodiment, due to the judgment at step 107, it is deemed that the amount (Qa) of NO_2 cold stored in the NO_x absorbent 47 when this temperature raising control is executed is made not more than the amount (Qb) of the NO_x storable in the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is raised to the temperature Td for activation. Therefore, according to this embodiment, it is possible to suppress the release of NO_2 cold stored in the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated and raise the temperature of the NO_x storing catalyst 11 to activate it. That is, it is possible to suppress the occurrence of the seepage phenomenon. Note that theoretically, by doing this, the release of NO_2 which had been cold stored is prevented at the time of raising the temperature of the NO_x storing catalyst 11 to activate it, but in fact it is difficult to completely prevent the release of NO_2 as NO_x . Therefore, in

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actuality, by providing the judgment at step 107, the amount of release of NO₂ when released as NO_x or the amount of release per unit time is prevented from being more than a predetermined set amount.

5 When the temperature raising control is started at step 109, the routine proceeds to step 111, where it is judged if the temperature rise of the NO_x storing catalyst 11 has finished. That is, for example, when the temperature TC of the NO_x storing catalyst 11 becomes the
10 temperature Td or more, it is judged that the temperature rise has finished. In this embodiment, the temperature detected by the temperature sensor 20 is used for this judgment. When it is judged at step 111 that the
15 temperature rise of the NO_x storing catalyst 11 has not finished, the routine returns to step 109, where the temperature raising control is continued. On the other hand, when it is judged that the temperature rise of the NO_x storing catalyst 11 has finished, the routine
20 proceeds to step 113, where the temperature raising control is ended and the routine proceeds to step 115.

 At step 115, a NO_x release and reduction control for causing release of NO_x from the NO_x absorbent 47 and reducing it is executed. That is, while maintaining the state where the NO_x storing catalyst 11 is activated,
25 that is, while maintaining the temperature TC of the NO_x storing catalyst 11 at the temperature Td or more, the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst 11 is made smaller and the presence of a reducing agent is established. More specifically, in this
30 embodiment, the air-fuel ratio in the combustion chamber 2 is made rich or the stoichiometric air-fuel ratio or reducing agent is supplied from the reducing agent supply valve 13 so as to maintain the temperature TC of the NO_x storing catalyst 11 at the temperature Td or more and
35 intermittently or continuously make the air-fuel ratio of the exhaust gas rich or the stoichiometric air-fuel ratio. By doing this, the NO_x is released from the NO_x

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absorbent 47 and the released NO_x is reduced and purified by the reducing agent (unburned HC, CO, etc.) present in the exhaust gas.

When the above-mentioned NO_x release and reduction control is started at step 115, the routine proceeds to step 117, where it is judged if the release of NO_x from the NO_x absorbent 47 has been completed. This judgment is made by finding in advance the NO_x release speed (amount of release of NO_x per unit time) from the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is the above temperature Td by experiments etc. and judging if the released NO_x amount in the current NO_x release and reduction control estimated from the NO_x release speed and the duration of the NO_x release and reduction control has become greater than the NO₂ stored amount estimated at step 101. That is, it is judged that the release of NO_x has been completed when it is judged that the above estimated released NO_x amount has become greater than the NO₂ stored amount estimated at step 101.

At step 117, when it is judged that the release of NO_x from the NO_x absorbent 47 has still not been completed, the routine returns to step 115 where the NO_x release and reduction control is continued. On the other hand, when it is judged that the release of NO_x from the NO_x absorbent 47 has been completed, the routine proceeds to step 119 where the NO_x release and reduction control is ended and the control routine is ended.

As explained above, by this method, the temperature raising control is started when the estimated NO₂ stored amount Qa has become greater than or equal to the judgment criteria amount Qx set to not more than the NO_x storable amount Qb based on the NO_x storable amount Qb of the NO_x absorbent 47 at the time when the temperature TC of the NO_x storing catalyst 11 is the temperature Td. Therefore, it is possible to suppress the release of NO_x occurring when cold stored NO₂ can not be completely stored when the temperature TC of the NO_x storing

catalyst 11 is raised to the temperature Td and the catalyst is activated. That is, according to this method, it is possible to suppress release of NO₂ cold stored in the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated and raise the temperature of the NO_x storing catalyst 11 for activation. That is, it is possible to suppress the occurrence of the above seepage phenomenon. Further, with this method, a NO_x release and reduction control is executed, so it is possible to get NO_x released from the NO_x absorbent 47 and reduce and purify it.

In this way, according to this method, it is possible to suppress the occurrence of the seepage phenomenon and use the NO_x storing catalyst 11 to purify the NO₂ in the exhaust gas and suppress the release of NO_x into the atmosphere.

Next, another method workable by the configuration shown in FIG. 1, that is, another method of suppressing the occurrence of the seepage phenomenon explained above and using the NO_x storing catalyst 11 to purify NO₂ in the exhaust gas and suppress the release of NO_x into the atmosphere will be explained with reference to FIG. 7. Note that this method includes parts common with the method explained with reference to FIG. 5. Explanations of these parts will in principle be omitted.

If the NO_x release speed (amount of release of NO_x per unit time) when cold stored NO₂ is released from the NO_x absorbent 47 when making the temperature TC of the NO_x storing catalyst 11 the temperature Td for the NO_x release and reduction control is less than or equal to the storing speed of NO_x (amount of storage of NO_x per unit time) to the NO_x absorbent 47 when making the temperature TC of the NO_x storing catalyst 11 the temperature Td, release of cold stored NO₂ may not substantially occur when raising the temperature TC of the NO_x storing catalyst 11 to the temperature Td to activate the catalyst. The method explained below is

based on this thinking.

Note that in the state where the temperature TC of the NO_x storing catalyst 11 becomes the temperature Td and the NO_x storing catalyst 11 is activated, the NO_x in the exhaust gas is mainly hot stored at the NO_x absorbent 47, but in this case as well, it cannot be said that there is no cold storing at all. That is, in the state where the NO_x storing catalyst 11 is activated, the NO_x in the exhaust gas is stored in the NO_x absorbent 47 (including meanings of both cold storing and hot storing).

FIG. 7 is a flow chart showing the control routine of this method. This control routine is executed by interruption every certain time by the ECU 30 at the time of normal operation of the engine. When this control routine starts, first, at step 201, the NO₂ stored amount Qa at that point of time is estimated. The control at step 201 is similar to the control at step 101 of FIG. 5.

When the NO₂ stored amount Qa is estimated at step 201, the routine proceeds to step 203. At step 203, the release speed Va of NO_x from the NO_x absorbent 47 in the case where the temperature TC of the NO_x storing catalyst 11 is the predetermined temperature Td is estimated. Here, the temperature Td is the temperature predetermined as the temperature for performing the NO_x release and reduction control performed later and is greater than or equal to the temperature where the activation of the NO_x storing catalyst 11 is at least started (activation temperature), in the same way as the case explained with reference to FIG. 5.

The NO_x release speed Va is estimated based on for example the temperature Td and the NO₂ stored amount Qa. That is, the relationship between the amount of NO_x including the NO₂ cold stored in the NO_x absorbent 47 (NO_x stored amount) and the amount of NO_x released from the NO_x absorbent 47 per unit time (NO_x release speed) becomes a relationship where the NO_x release speed

becomes larger the greater the NO_x stored amount as shown in FIG. 8a when the temperature of the NO_x storing catalyst 11 is constant. Therefore, if finding in advance the relationship such as shown in FIG. 8a for when the temperature TC of the NO_x storing catalyst 11 is the above temperature Td, by using the NO_2 stored amount Qa estimated at step 201 as the NO_x stored amount, it is possible to find the corresponding NO_x release speed, that is, the NO_x release speed Va to be found.

When the NO_x release speed Va is estimated at step 203, the routine proceeds to step 205. At step 205, the storing speed Vb of NO_x to the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is the temperature Td is estimated. The NO_x storing speed Vb is for example estimated based on the temperature Td and NO_2 stored amount Qa in the same way as the case of estimation of the NO_x release speed Va. That is, the relationship between the amount of NO_x including the NO_2 cold stored in the NO_x absorbent 47 (NO_x stored amount) and the amount of NO_x including NO_2 cold stored in the NO_x absorbent 47 per unit time (NO_x storing speed) becomes the relationship where the NO_x storing speed becomes smaller the larger the NO_x stored amount as shown in FIG. 8b when the temperature of the NO_x storing catalyst 11 is constant. Therefore, if finding in advance the relationship such as shown in FIG. 8b for when the temperature TC of the NO_x storing catalyst 11 is the above temperature Td, by using the NO_2 stored amount Qa estimated at step 201 as the NO_x stored amount, it is possible to find the corresponding NO_x storing speed, that is, the NO_x storing speed Vb to be found.

When the NO_x storing speed Vb is estimated at step 205, at the next step 207, the judgment criteria speed Vx is calculated based on the NO_x storing speed Vb. This judgment criteria speed Vx is used in the later step 209 and is found for example by the equation $Vx = Vb - \beta$ (where

$\beta \geq 0$). Here, the constant β is a safety margin for suppressing the occurrence of the above-mentioned seepage phenomenon and can be suitably set.

When the judgment criteria speed V_x is calculated at
5 step 207, the routine proceeds to step 209. At step 209,
it is judged if the NO_x release speed V_a is the judgment
criteria speed V_x or more. When it is judged here that
the NO_x release speed V_a is less than the judgment
10 criteria speed V_x , the control routine is ended and the
engine continues normal operation. On the other hand,
when it is judged that the NO_x release speed V_a is the
judgment criteria speed V_x or more, the routine proceeds
to step 211, where the temperature raising control and
the NO_x release and reduction control are executed. Note
15 that the control at step 211 is similar to the controls
from step 109 to step 119 of FIG. 5, so an explanation
will be omitted.

As explained above, by this method, the temperature
raising control (and succeeding NO_x release and reduction
20 control) is executed when the NO_x release speed V_a when
the temperature T_C of the NO_x storing catalyst 11 is the
temperature T_d becomes greater than or equal to the
judgment criteria speed V_x set to not more than the NO_x
storing speed V_b based on the NO_x storing speed V_b when
25 the temperature T_C of the NO_x storing catalyst 11 is the
temperature T_d . Therefore, it is possible to suppress the
release of NO_x to the atmosphere - believed to occur as a
result of the NO_x release speed becoming larger than the
 NO_x storing speed when the temperature T_C of the NO_x
30 storing catalyst 11 is raised to the temperature T_d and
the catalyst is activated. That is, according to this
method, it is possible to substantially suppress the
release from the NO_x absorbent 47 of the NO_2 cold stored
in the NO_x absorbent 47 in the state where the NO_x
35 storing catalyst 11 is not activated and raise the
temperature of the NO_x storing catalyst 11 to activate
it. That is, it is possible to suppress the occurrence of

the above seepage phenomenon. Further, in this method as well, the NO_x release and reduction control is executed, so it is possible to get NO_x released from the NO_x absorbent 47 and reduce and purify it.

5 As explained above, by this method as well, in the same way as the method explained with reference to FIG. 5, it is possible to suppress the occurrence of the seepage phenomenon explained above and use the NO_x storing catalyst 11 to purify the NO₂ in the exhaust gas
10 so as to suppress emission of NO_x into the atmosphere.

Next, still another method able to be worked by the configuration shown in FIG. 1, that is, still another method to suppress the occurrence of the seepage
phenomenon explained above and use the NO_x storing
15 catalyst 11 to purify the NO₂ in the exhaust gas so as to suppress emission of NO_x into the atmosphere, will be explained with reference to FIG. 9. Note that this method includes parts common with the methods explained
previously with reference to FIG. 5 and FIG. 7. The
20 explanations of these parts will in principle be omitted.

As explained above, if the NO_x release speed (amount of release of NO_x per unit time) when cold stored NO₂ is released from the NO_x absorbent 47 when making the
temperature TC of the NO_x storing catalyst 11 the
25 temperature Td for the NO_x release and reduction control is less than or equal to the NO_x storing speed (amount of storing of NO_x per unit time) to the NO_x absorbent 47
when making the temperature TC of the NO_x storing
catalyst 11 the temperature Td, it is believed that no
30 release of cold stored NO₂ substantially occurs when raising the temperature TC of the NO_x storing catalyst 11 to the temperature Td to activate the catalyst. However, even in this case, the NO_x exhausted from the internal
combustion engine may end up being released into the
35 atmosphere. The method explained below attempts to further suppress the release of NO_x into the atmosphere considering also the NO_x exhausted from the internal

combustion engine during such a temperature raising control etc.

FIG. 9 is a flow chart showing the control routine of this method. This control routine is executed by interruption every certain time by the ECU 30 at the time of normal operation of the engine. When this control routine starts, first, at step 301, the NO₂ stored amount Qa at that point of time is estimated. The control at step 301 is similar to the control at step 101 of FIG. 5 and step 201 of FIG. 7.

When the NO₂ stored amount Qa is estimated at step 301, the routine proceeds to step 303. At step 303, the release speed Va of NO_x from the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is the predetermined temperature Td is estimated. The control at step 303 is similar to the control at step 203 of FIG. 7.

Next, at step 305, the speed of production of NO_x by combustion in the internal combustion engine, that is, the NO_x exhaust speed (amount of NO_x exhaust per unit time) Ve from the internal combustion engine, is estimated. The NO_x exhaust speed Ve from the internal combustion engine is estimated based on for example the operating state of the internal combustion engine. In this case, for example, the engine speed and the fuel injection amount are used as indicators expressing the operating state. The NO_x exhaust speed Ve in each operating state expressed by these is found in advance by experiments etc. and stored as a map. The map is used to find the NO_x exhaust speed Ve based on the operating state at any particular time.

When the NO_x exhaust speed Ve is estimated at step 305, the routine proceeds to step 307. At step 307, the NO_x storing speed Vb to the NO_x absorbent 47 when the temperature TC of the NO_x storing catalyst 11 is the temperature Td is estimated. Further, when the NO_x storing speed Vb is estimated at step 307, at the next step 309, the judgment criteria speed Vx used at step 311

is calculated based on the NO_x storing speed Vb (for example, $Vx = Vb - \beta$ (where $\beta \geq 0$)). The controls at these steps 307 and 309 are similar to the controls at steps 205 and 207 of FIG. 7, respectively.

5 When the judgment criteria speed Vx is calculated at step 309, the routine proceeds to step 311. At step 311, it is judged if the sum (Va+Ve) of the NO_x release speed Va and the NO_x exhaust speed Ve is the judgment criteria speed Vx or more. When it is judged here that the sum of
10 the NO_x release speed Va and the NO_x exhaust speed Ve is less than the judgment criteria speed Vx, this control routine ends and the engine continues normal operation. On the other hand, when it is judged that the sum of the NO_x release speed Va and the NO_x exhaust speed Ve is the
15 judgment criteria speed Vx or more, the routine proceeds to step 313, where the temperature raising control and the NO_x release and reducing control are executed. Note that the control at step 313 is similar to the control of step 211 of FIG. 7, that is, similar to the controls from
20 step 109 to step 119 of FIG. 5, so an explanation is omitted here.

As explained above, by this method, the temperature raising control (and succeeding NO_x release and reduction control) is executed when the sum of the NO_x release
25 speed Va when the temperature TC of the NO_x storing catalyst 11 is the temperature Td and the NO_x exhaust speed Ve from the internal combustion engine becomes greater than or equal to the judgment criteria speed Vx set to not more than the NO_x storing speed Vb based on
30 the NO_x storing speed Vb when the temperature TC of the NO_x storing catalyst 11 is the temperature Td. Therefore, it is possible to suppress the release of NO_x to the atmosphere - believed to occur as a result of the NO_x release speed becoming larger than the NO_x storing speed
35 when the temperature TC of the NO_x storing catalyst 11 is raised to the temperature Td and the catalyst is activated, and to suppress the release into the

atmosphere of the NO_x exhausted from the internal combustion engine as well. That is, according to this method, it is possible to substantially suppress the release from the NO_x absorbent 47 of the NO_2 cold stored in the NO_x absorbent 47 in the state where the NO_x storing catalyst 11 is not activated, suppress the release of NO_x exhausted from the internal combustion engine into the atmosphere, and raise the temperature of the NO_x storing catalyst 11 to activate it. That is, it is possible to suppress the occurrence of the above seepage phenomenon and possible to suppress the release of NO_x exhausted from the internal combustion engine into the atmosphere during the temperature raising control etc. Further, in this method as well, the NO_x release and reduction control is executed, so it is possible to get NO_x released from the NO_x absorbent 47 and reduce and purify it.

As explained above, by this method as well, in the same way as the method explained with reference to FIG. 5 and FIG. 9, it is possible to suppress the occurrence of the seepage phenomenon explained above and use the NO_x storing catalyst 11 to purify the NO_2 in the exhaust gas so as to suppress emission of NO_x into the atmosphere.

FIG. 10 is an explanatory view showing the relationship among the NO_x release speed V_a , NO_x exhaust speed V_e , NO_x storing speed V_b , judgment criteria speed V_x , etc. indicating the NO_2 stored amount Q_a on the abscissa. When based on FIG. 10, in the method explained with reference to FIG. 7, the temperature raising control (and succeeding NO_x release and reduction control) is executed when the NO_2 stored amount Q_a becomes Q_{a1} or more, while in the method explained with reference to FIG. 9, the temperature raising control (and succeeding NO_x release and reduction control) is executed when the NO_2 stored amount Q_a becomes Q_{a2} or more.

However, as explained above, the nitrogen dioxide NO_2 contained in the exhaust gas is cold stored in the

NO_x absorbent 47 even if the NO_x storing catalyst 11 is not activated, but the nitrogen monoxide NO contained in the exhaust gas is not stored in the NO_x absorbent 47 unless the NO_x storing catalyst 11 is activated and it is oxidized to nitrogen dioxide NO₂. Therefore, when the NO_x storing catalyst 11 is not activated, it is preferable to reduce the amount of nitrogen monoxide NO in the exhaust gas and increase the amount of nitrogen dioxide NO₂ in the exhaust gas. Therefore, in an embodiment of the present invention, the ratio of the nitrogen dioxide NO₂ to the nitrogen monoxide NO produced at the time of combustion under a lean air-fuel ratio when the NO_x storing catalyst 11 is not activated may be increased compared with when the NO_x storing catalyst 11 is activated under the same engine operating state, that is, the same speed and same torque.

It becomes clear that the ratio of NO₂ (amount of NO₂/amount of NO) increases when burning the fuel gently. If for example employing at least one of delay of the fuel injection timing, increase of the amount of EGR gas, pilot injection, or premixed combustion, the combustion becomes gentler. Therefore, when increasing the amount of nitrogen dioxide NO₂ in the exhaust gas such as explained above in the embodiments of the present invention, at least one of the above techniques for achieving gentler combustion is adopted when the NO_x storing catalyst 11 is not activated so as to achieve gentler combustion compared with when the NO_x storing catalyst is activated in the same engine operating state.

Note that in the above explanation, the temperature raising control was performed by controlling the fuel injection patterns, but the invention is not limited to this. For example, it is also possible to use an electric heater or use another means to raise the temperature of the NO_x storing catalyst 11.

While the invention has been described with reference to specific embodiments chosen for purpose of

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illustration, it should be apparent that numerous modifications could be made thereto by those skilled in the art without departing from the basic concept and scope of the invention.

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CLAIMS

1. An exhaust purification device for an internal combustion engine having, a NO_x storing catalyst arranged in an engine exhaust passage, the NO_x storing catalyst
5 being comprised of a precious metal catalyst and a NO_x absorbent and, when an air-fuel ratio of inflowing exhaust gas is lean, cold storing nitrogen dioxide NO₂ contained in the exhaust gas in the NO_x absorbent when not activated and hot storing cold stored nitrogen
10 dioxide NO₂ in the NO_x absorbent when activated,
said exhaust purification device for an internal combustion engine making the nitrogen dioxide NO₂ contained in the exhaust gas be cold stored in the NO_x absorbent in the state where said NO_x storing
15 catalyst is not activated and executing a NO_x storing catalyst restoring control including at least raising the temperature of said NO_x storing catalyst to a predetermined temperature to activate it when a predetermined NO_x storing catalyst restoring condition is
20 met so as to restore the cold storing capability of said NO_x absorbent in the state where said NO_x storing catalyst is not activated.
2. An exhaust purification device as set forth in claim 1, wherein said NO_x storing catalyst restoring
25 condition is set to be met before the cold storing capability of said NO_x absorbent in the state where said NO_x storing catalyst is not activated is saturated.
3. An exhaust purification device as set forth in claim 1, wherein said NO_x storing catalyst restoring
30 condition is set so that the cold stored nitrogen dioxide NO₂ will not be released from said NO_x absorbent in more than a predetermined amount when raising the temperature of and activating said NO_x storing catalyst in said NO_x storing catalyst restoring control.
- 35 4. An exhaust purification device as set forth in claim 1, wherein
said device has a NO₂ stored amount

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estimating means for estimating an amount of nitrogen dioxide NO₂ cold stored in said NO_x absorbent and a NO_x storable amount estimating means for estimating an amount of nitrogen oxides NO_x able to be stored in said NO_x absorbent when said NO_x storing catalyst is at said predetermined temperature and

5 said NO_x storing catalyst restoring condition is deemed to be met when the NO₂ stored amount estimated by said NO₂ stored amount estimating means
10 becomes greater than or equal to a predetermined amount set to not more than said NO_x storable amount based on the NO_x storable amount estimated by said NO_x storable amount estimating means.

15 5. An exhaust purification device as set forth in claim 1, wherein

said NO_x storing catalyst is a NO_x storing catalyst having the function of hot storing nitrogen oxides NO_x contained in exhaust gas in the NO_x absorbent when said NO_x storing catalyst is activated and the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst is lean,

20 said device has a NO_x release speed estimating means for estimating a release speed of nitrogen oxides NO_x from said NO_x absorbent when making
25 said NO_x storing catalyst said predetermined temperature and a NO_x storing speed estimating means for estimating a storing speed of nitrogen oxides NO_x to said NO_x absorbent when making said NO_x storing catalyst said predetermined temperature, and

30 said NO_x storing catalyst restoring condition is deemed to be met when the NO_x release speed estimated by said NO_x release speed estimating means becomes greater than or equal to a predetermined speed set to not more than said NO_x storing speed based on the
35 NO_x storing speed estimated by said NO_x storing speed estimating means.

6. An exhaust purification device as set forth in

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claim 1, wherein

said NO_x storing catalyst is a NO_x storing catalyst having the function of hot storing nitrogen oxides NO_x contained in exhaust gas in the NO_x absorbent when said NO_x storing catalyst is activated and the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst is lean,

said device has a NO_x release speed estimating means for estimating a release speed of nitrogen oxides NO_x from said NO_x absorbent when making said NO_x storing catalyst said predetermined temperature, a NO_x exhaust speed estimating means for estimating an exhaust speed of nitrogen oxides NO_x from the internal combustion engine, and a NO_x storing speed estimating means for estimating a storing speed of nitrogen oxides NO_x to said NO_x absorbent when making said NO_x storing catalyst said predetermined temperature, and

said NO_x storing catalyst restoring condition is deemed to be met when a sum of the NO_x release speed estimated by said NO_x release speed estimating means and the NO_x exhaust speed estimated by said NO_x exhaust speed estimating means becomes greater than or equal to a predetermined speed set to not more than said NO_x storing speed based on the NO_x storing speed estimated by said NO_x storing speed estimating means.

7. An exhaust purification device as set forth in claim 1, wherein

said NO_x storing catalyst has the function of releasing, reducing, and purifying the nitrogen oxides NO_x which had been hot stored in the NO_x absorbent when said NO_x storing catalyst is activated and when making the air-fuel ratio of the exhaust gas flowing into the NO_x storing catalyst smaller and establishing the presence of a reducing agent in state, and

said NO_x storing catalyst restoring control includes making the air-fuel ratio of the exhaust

gas flowing into the NO_x storing catalyst smaller and establishing the presence of a reducing agent in state.

5 8. An exhaust purification device as set forth in claim 1, further having a NO₂ ratio increasing means for increasing a ratio of nitrogen dioxide NO₂ with respect to nitrogen monoxide NO produced at the time of combustion under a lean air-fuel ratio when said NO_x storing catalyst is not activated compared with when the NO_x storing catalyst is activated in the same engine
10 operating state.

 9. An exhaust purification method for an internal combustion engine including, arranging a NO_x storing catalyst in an engine exhaust passage, the NO_x storing catalyst being comprised of a precious metal catalyst and
15 a NO_x absorbent and, when an air-fuel ratio of inflowing exhaust gas is lean, cold storing nitrogen dioxide NO₂ contained in the exhaust gas in the NO_x absorbent when not activated and hot storing cold stored nitrogen dioxide NO₂ in the NO_x absorbent when activated,
20 making the nitrogen dioxide NO₂ contained in the exhaust gas be cold stored in the NO_x absorbent in the state where said NO_x storing catalyst is not activated and raising the temperature of said NO_x storing catalyst to a predetermined temperature to activate it so
25 as to restore the cold storing capability of said NO_x absorbent in the state where said NO_x storing catalyst is not activated before the cold storing capability of said NO_x absorbent in the state where said NO_x storing catalyst is not activated is saturated.